

Photochemical formation rates of organic aerosols through time-resolved *in situ* laboratory measurements

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ABSTRACT

The presence of photochemically-generated hazes has a significant impact on radiative transfer in planetary atmospheres. For Titan and the giant planets, rates of particle formation have been inferred from photochemical or microphysical models constrained to match Voyager observations, yet these rates have not been determined experimentally. Models of these atmospheres and of potential hazes in Earth's early atmosphere which may have served as a UV-shield (thus protecting photo-labile greenhouse gases and organic compounds) include a number of approximations, some of them quite arbitrary, for the overall rate of photochemically-driven particle formation. We have developed instrumentation for simultaneously measuring the net production rates of complex gas-phase hydrocarbons and of organic aerosols formed from irradiating mixtures of simple precursor gases through online quadrupole mass spectrometry measurements of gas-phase species and *in situ* optical scattering detection of the particulates at 633nm. The new technique and results for the generation of hydrocarbon aerosol from the irradiation of pure, gas-phase CH₄ with vacuum ultraviolet light (120-300nm) are discussed.

1. Introduction

Photochemically-generated aerosols are a common component of planetary atmospheres and are as diverse as the hydrocarbon Axel-Danielson dust of the giant planets, the complex organic hazes on Titan, the sulfuric acid aerosol in the atmospheres of Earth and Venus today, and the hydrocarbon hazes hypothesized to have existed under very different atmospheric conditions in Earth's past. The presence of these aerosols significantly alters atmospheric radiative transfer. Depending on their altitude, size distribution, and chemical composition, for example, they may warm or cool the atmosphere or the surface, and they may induce dynamical feedbacks. On the giant planets, the presence of hydrocarbon aerosol is responsible for these planets' stratospheres [e.g. *Yung and DeMore*, 1999], while on Titan, the haze is thought to cool the surface by an "antigreenhouse effect" [*McKay et al.*, 1991]. For the early Earth and terrestrial-like extrasolar planets, complex feedbacks between radiation, gas-phase chemistry, particle formation, and dynamics likely play(ed) a key role in determining climate and habitability.

On Titan and the giant planets, these hazes are known to be composed of hydrocarbon particulates that are photochemically formed from gaseous precursors. While the rates of particle formation have been inferred from photochemical or microphysical models constrained to match Voyager observations of geometric albedo or thermal emission [e.g., *McKay et al.*, 1989; *Samuelson and Mayo*, 1991; *Toon et al.*, 1992; *Rannou et al.*, 1995], these rates have not been determined experimentally. Thus, the fundamental kinetics of particle formation and the mechanism for polymerization of hydrocarbons to form condensable species are not known [*Yung and DeMore*, 1999], and these processes remain highly parameterized in planetary atmospheric models. Moreover, the particle formation rates inferred from Titan's geometric albedo are highly dependent on the index of refraction derived from particles created in the laboratory and measured after the particles are deposited as a film [*Ramirez et al.*, 2002]. These laboratory values are routinely scaled

by factors of 0.5 to 3 in order to match observations of Titan [see, *e.g.*, *McKay et al.*, 2001]. Thus, uncertainties in both formation rates of particles and their optical properties make new approaches to quantifying polymerization rates and measuring the index of refraction of Titan-like hazes highly desirable.

For the early Earth, photochemical models suggest that photolysis of CH_4 , produced biotically in an atmosphere of CO_2 , N_2 , and water vapor, could have produced a photochemical haze [*e.g.*, *Kasting et al.*, 1983; *Zahnle*, 1986; *Pavlov et al.*, 2000; *Pavlov et al.*, 2001a; *Pavlov et al.*, 2001b]. *Sagan and Chyba* [1997] proposed that such a haze layer may have shielded the lower atmosphere from UV radiation and could therefore have significantly warmed Earth's surface by protecting the UV-labile greenhouse gas NH_3 from rapid destruction. The presence of the haze, they argued, might thus help to resolve the question of how Earth maintained liquid water on its surface billions of years ago despite a "fainter" Sun and geologic evidence that CO_2 concentrations were too low to produce a sufficient greenhouse effect alone. The UV-shielding aerosol could also have protected organic molecules at the surface prior to the rise in atmospheric oxygen and hence, the formation of an ozone layer [*see also Lovelock*, 1988]. In contrast, *Pavlov et al.* [2001] and *McKay et al.* [1991, 1999] have shown that whether or not such a haze warmed or cooled the surface or even served as an early UV-shield depends on the chemical composition and size distribution of the aerosol. Both of their studies suggest that a haze more likely cooled the surface, thus exacerbating the so-called "faint young sun paradox" rather than contributing to its solution. Furthermore, modeling by *Pavlov et al.* [2001] suggests that the size distribution of particulates was such that the aerosol would likely not have formed a UV-shield either. The models used to predict the formation of a haze layer on early Earth and its chemical and optical properties, however, include a number of approximations, some of them quite arbitrary, for the rates of particle formation. In addition, the models are sensitive to the atmospheric CH_4/CO_2 ratio and predict that CH_4 begins to polymerize (rather than oxidize) when this ratio exceeds unity [*Pavlov et al.*, 2000; *Pavlov et al.*, 2001; *Zahnle*

1986], yet no laboratory data exist to test these predictions. Thus, uncertainties in both formation rates of aerosols and their optical properties limit our understanding of the potential feedbacks between atmospheric chemistry, radiation, and climate during Earth's first 2 billion years of history. Moreover, because there can be no direct observations of early Earth's atmosphere, these limitations are even more severe than those for Titan's current atmosphere.

To provide new time-resolved laboratory data on photochemical particle formation kinetics that may be applied to a variety of planetary atmospheres, we have developed instrumentation to simultaneously measure the evolution of both gas-phase species and the production of particles *in situ* in the reaction chamber during UV irradiation. Although a number of laboratory simulations producing solid particles thought to be similar to Titan's aerosol have been performed in which mixtures of gases have been subjected to VUV light, plasma discharge, or energetic electrons [*e.g.*, Khare *et al.*, 1984 and references therein; Khare *et al.*, 1987; Coll *et al.*, 1999; Clarke and Ferris; 1997], characterization of the particles or higher hydrocarbon gas-phase species was done "off-line." That is, the resulting solids have been collected as a film on a slide for determination of particle chemical and optical properties. For example, indices of refraction have been determined from transmittance, reflectance, interference, and polarization measurements [*e.g.*, Khare 1984; Ramirez *et al.*, 2002]. Particle sizes and shapes have been characterized using scanning electron microscopy (SEM) [*e.g.*, Khare *et al.*, 1984; Coll *et al.*, 1999; de Vanssay *et al.*, 1999]. The presence of various chemical functional groups has been obtained through IR spectra of the films [*e.g.*, McDonald *et al.*, 1994; Coll *et al.*, 1999; Ferris and Clarke 1997]. For analysis of complex gas phase species formed by a cold plasma discharge that also produced an unmeasured flux of UV and visible light, Coll *et al.* [1999] cryogenically collected the gaseous products remaining after particle formation and analyzed them using gas chromatography/mass spectrometry. In contrast to all of these studies, our new *in situ* technique enables purely photochemical formation rates to be monitored continuously as a function of irradiation time for both the aerosol (through optical

scattering measurements) and complex gas-phase species (through online quadrupole mass spectrometry). In addition, modifications to the apparatus to detect the optical scattering from particles as a function of scattering angle will allow the index of refraction and size distribution of the aerosols to ultimately be derived from *in situ* measurements while the particles are still suspended in the gas phase rather than from particles which have settled onto a substrate in films of varying thickness. Thus, the technique demonstrated here with "proof-of-concept" measurements for the formation of particulates from the UV photolysis of pure, gas-phase CH₄ represents a unique new probe of the photochemical kinetics of particle condensation from gas-phase species. These and future results will serve as new constraints for photochemical and microphysical models of aerosols in planetary atmospheres.

2 Experiment description and measurements

The apparatus consists of three main components: an ultra-high vacuum reaction chamber with a VUV irradiation source, an online mass spectrometer for measuring gas-phase species, and a light source, optics, and detector for measuring optical scattering from particles (Figure 1). In short, VUV light drives photochemistry within the reaction chamber while a residual gas analysis (RGA) mass spectrometer monitors the time evolution of gas-phase species and photon-counting of scattered light provides an *in situ* measurement of the optical scattering from photochemically-produced particulates.

2.1 Reaction chamber and experimental protocol: The VUV irradiation source is an air-cooled 30W deuterium lamp (Hamamatsu L2D2 7292) mounted directly onto the vacuum chamber. Total lamp intensity, measured using standard N₂O actinometry [Greiner, 1967], is $8.8 \pm 0.8 \times 10^{15}$ photons s⁻¹ from 120 to 300 nm, with maximum output near 160nm. Reactant gas enters the chamber through a valved inlet. For experiments using mixtures of gases, the gases are either pre-mixed or introduced through a system of flow controllers and tubing designed to assure turbulent

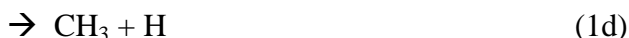
mixing of gases even when the mixing ratios of components differ by orders of magnitude. The total pressure in the reaction chamber is measured with both a cold-cathode gauge (Pfeiffer) and a capacitance manometer (MKS). When evacuated, the chamber has a background pressure of 10^{-8} Torr from H_2 (10^{-8} Torr) and H_2O (10^{-9} Torr), as measured by the RGA.

For the experiments presented here for irradiation of CH_4 , the experimental protocol was as follows. Each ~60 hour irradiation began by pumping the apparatus down to its background pressure of 10^{-8} Torr and measuring background signals for the optical scattering and RGA mass spectrometer. The reaction chamber was then isolated from the turbomolecular pump (Pfeiffer) and filled with high purity CH_4 (Matheson, 99.99%). Another background dataset was recorded prior to irradiation, and then the deuterium lamp was turned on. Optical scattering and RGA signals were processed and recorded under PC control, along with housekeeping data for the system. For the static run of CH_4 at 70 Torr presented here, the total pressure in the reaction chamber changed by less than 1% during the course of the experiment in response to long term thermal fluctuations in the laboratory. After irradiation, the vacuum seal was broken in order to clean a brown film off the MgF_2 window of the deuterium lamp. The chamber was then pumped down to its base pressure for the next experimental run.

2.2 Online mass spectrometer: An RGA quadrupole mass spectrometer (Stanford Research Systems: RGA-200) is used to monitor the chemical evolution of all gas-phase species from 1 to 200 amu in the reaction chamber at 5 minute intervals. Since the RGA must operate at pressures below 10^{-4} Torr, a high precision leak valve (Kurt Lesker) is used to introduce gas from the chamber into the RGA analysis region continuously throughout the experiment. The detection limit in the partial pressure units reported by the RGA is 10^{-10} Torr, giving a sensitivity to all other gas-phase species of 10^{-6} relative to CH_4 (at 10^{-4} Torr in the RGA) in the experiments reported here.

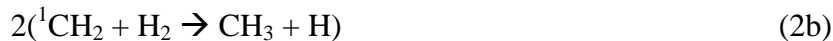
Results for the time evolution of gas-phase species for irradiation of CH₄ at a pressure of 70 Torr are shown in Figures 2, 3, and 4. The data in Figure 2 are the actual mass scans, reported in partial pressures and plotted at one-hour intervals for clarity. Note that due to electron impact mass fragmentation patterns of hydrocarbons, the intensity of the signals at some m/z values are the result of fragment ions from several different parent species. For example, the signal at m/z = 26 is primarily composed of contributions from C₂H_{2n} species for n= 1, 2, 3 as well as small contributions from the less abundant C₃H₄ and C₄H₁₀ species. Moreover, the raw partial pressures plotted in Figure 2 are sensitive to the identity of the gas due to ionization detection efficiencies. Both the fragmentation patterns and the sensitivity factors for individual gases are calibrated after each experiment using pure laboratory standards for H₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₈ and C₄H₁₀. For C₃H₄ and C₄H₂, we use fragmentation patterns from the NIST database [Stein, 2001]. The calibrations are then used to deconvolve the raw data in Figure 2 into the calibrated partial pressures shown in Figure 3. Time series showing the net production of gas-phase species in units of mixing ratios and concentrations in the reaction chamber (Figure 4) are then calculated using the calibrated partial pressures in Figure 3 and measurements of the total pressure in the reaction chamber.

Figures 2, 3 and 4a show that H₂ increases with irradiation time, as expected as CH₄ is photolyzed and higher hydrocarbons are formed. For example, the radicals formed from CH₄ photolysis (reaction 1)



such as ¹CH₂ and CH₂ (which are the first excited and ground electronic states, respectively, of the methylene radical) can go on to form C₂ and higher hydrocarbons. One mechanism for producing

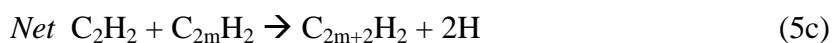
ethane (C₂H₆) starting with CH₄ photolysis is shown in reaction scheme 2, for which there is a net increase of two hydrogen atoms:



Net reactions for the formation of C₂H_{2n} from CH₄ for n = 1 (acetylene) and 2 (ethylene) are:



These C₂H_{2n} species may then go on to produce C_mH_n hydrocarbons, such as polyacetylenes, C_{2m+2}H₂:



In each of these gas-phase pathways to higher hydrocarbons, two hydrogen atoms or one hydrogen molecule is produced for each new C-C bond formed [see, *e.g.*, *Yung and DeMore*, 1999].

The observed increase in H₂ is accompanied by increases in ethane and butane (C₄H₁₀) (Fig 3, 4d and g). Acetylene (C₂H₂) and ethylene (C₂H₄) increase and decrease only slightly, respectively, as expected if photochemical production and destruction are approximately equal (as they are, for example, in Jupiter's atmosphere [*Yung and DeMore*, 1999]). Because no signal at m/z > 50 amu was detectable in these runs, only upper limits may be placed on the formation of

hydrocarbon species larger than C_4H_{10} . While larger gas-phase hydrocarbons may form as precursors to particulates, a net accumulation of these species above experimental detection limits is not observed in these runs.

2.3 *In situ* detection of optical scattering from particles: The optical scattering component of the experiment (Figure 5) uses a 1KHz mechanically chopped, 15mW, 632.8nm HeNe laser and fiber optic waveguides (Newport: F-MBD). Collimated HeNe light is coupled into and out of the fibers with standard optics (Oriel). The fiber optic waveguide enters the reaction chamber through an o-ring sealed vacuum fitting. Inside the reaction chamber, the light is collimated out of the fiber and passed through an adjustable polarizer (New Focus) with a parallel transmittance of 0.32 and a perpendicular transmittance of 5.3×10^{-5} , which yields an extinction ratio of 6000:1. The collection optics for the scattered light are mounted perpendicular to the incident radiation and are analogous to the input optics with the addition of a HeNe laser line bandpass filter (Newport). The output fiber waveguide is coupled directly into a photomultiplier tube (PMT, Hamamatsu: R928) operated at a bias voltage of 1.1 kV. The incident radiation, E_0 , is polarized perpendicular to the detection plane (XY). Thus, only photons polarized parallel to the detection plane reach the PMT. This geometry favors scattering from particles. The HeNe laser line filter ensures that only photons which are elastically scattered are measured. The interaction region is approximately 1 cm^3 , based on a 1 cm diameter laser beam and 1 cm diameter field of view for the detector. Scattered light is collected synchronously with the optical chopper and sorted into laser "on" and laser "off" bins (see Figure 6) using a multichannel scaler/averager (MSA, Stanford Research Systems: Model SR430). Figure 7 shows the optical scattering signal integrated over 3-minute laser "on" and "off" cycles as a function of irradiation time.

2.4 Offline scanning electron microscopy of particles: In addition to the *in situ* detection of aerosol formation by optical scattering, particles were collected during several runs by inserting a

silicon wafer inside the reaction chamber. Covering a portion of the wafer while inside the reaction chamber served as a control by 1) preventing particle deposition on the control region within the reaction chamber and 2) controlling for particle deposition on the wafer after removal from the reaction chamber. The particles collected on the wafer were analyzed by field emission scanning electron microscopy. Both spherical and fractal particles were observed on the portion of the wafer exposed in the chamber and ranged from approximately 0.2 to 3 microns in diameter (Figure 8). No particles or films were observed on the section of the wafer which was covered while in the chamber. Thus, these results are a qualitative confirmation that particles were produced photochemically in the reaction chamber. A more quantitative analysis of particle shape and size distribution in future experiments will require additional experimental controls to prevent possible oxidation or other alteration of the particles after removal from the chamber.

3. Analysis of results

The gas-phase evolution of higher hydrocarbons and H_2 (Figures 2, 3 and 4) and the optical scattering signal (Figure 7) are both consistent with the formation of hydrocarbon aerosol in the reaction chamber. This is confirmed by the offline SEM analysis of collected particles (Figure 8). The formation of a brown film on the MgF_2 window of the deuterium lamp which reduces the VUV output over the course of the experiment is added confirmation. As CH_4 is irradiated, higher hydrocarbons and H_2 are observed to form. As particulates are formed near the VUV window and then settle into the laser interaction region, the optical scattering signal grows in. However, some of the particulates coat the MgF_2 window, eventually reducing the VUV lamp intensity to a flux too small to drive particle formation or gas-phase chemistry. The optical scattering signal drops as the particle formation rate decreases with decreasing VUV intensity and the particles settle out, while gas-phase chemical production of H_2 , C_2H_6 , and C_4H_{10} begins to level off and then stops. In section 3.1 below, the gas-phase mass spectrometer data are used to derive net production rates for higher

hydrocarbons in the gas phase, as well as an overall rate of production of C-C bonds in particulate form. In section 3.2 below, we then check that these rates are roughly consistent with the observed optical scattering signal.

3.1 Mass spectrometer results: Rates for the net production of gas-phase hydrocarbons and H₂ can be determined from the time evolution of the individual species measured once the dependence of the rates on VUV light intensity is taken into account. We do so with a phenomenological model to fit our measurements as follows:

The rate for the net formation of H₂, or R_{f,H_2} , is proportional to the photolysis rate for CH₄, or j_{CH_4} , and is given by (eqn 6):

$$R_{f,H_2} \propto j_{CH_4} = \int_{\lambda_i}^{\lambda_f} \sigma(\lambda) I(\lambda) \phi(\lambda) d\lambda \quad (6)$$

where $\sigma(\lambda)$ is the absorption cross-section, $I(\lambda)$ is the radiation intensity, and $\phi(\lambda)$ is the quantum efficiency for photolysis and the product of these 3 terms is integrated over the wavelength range relevant for the experiment, λ_i to λ_f . Since $\sigma(\lambda)$, $\phi(\lambda)$ and the output spectrum of the lamp do not change during the experiment, this expression simplifies to $R_{f,H_2} \propto I$. To account for the lamp attenuation, the concentration of H₂ is modeled empirically by a fixed, first-order formation rate, R_{f,H_2} , which is dependent on the time-dependent irradiation intensity, $I(t)$. For simplicity, the time decay of the lamp intensity is assumed to be linear. Moreover, a linear decay yields a better fit to the H₂ data than the best fit exponential decay. In either case, a least squares analysis is used to derive $I(t)$. The resulting best fit for the time evolution of [H₂] is shown as a solid line in Figure 4a using the time-dependent lamp intensity in Figure 9. This lamp intensity profile, derived from the [H₂] data, is then used to derive the net formation rates for all species, again assuming first order kinetics. The modeled concentration profiles are shown as solid lines in Figure 4. The derived net gas-phase formation rates are given in Table 1.

Not surprisingly, the results indicate that gas-phase hydrocarbon formation is driven by the intensity of VUV light. Moreover, first order kinetics do not explain the time dependence of $[C_4H_{10}]$ and $[C_2H_6]$. Comparison of the measured and modeled concentration profiles for C_4H_{10} (Figure 4g) shows that the net production of C_4H_{10} stops at about 40 hours of irradiation while H_2 is still being produced until the modeled lamp intensity (derived from the H_2 data) goes to zero at ~56 hours. Similarly, the C_2H_6 concentration (Figure 4d) levels off at ~45 hours of irradiation. The difference suggests that larger hydrocarbons are the first to stop increasing in concentration in response to decreasing irradiation intensity. This trend apparently extends to still larger hydrocarbons in particulate form since the optical scattering signal from particles (Figure 7) no longer increases after ~35 hours of irradiation.

To a first approximation, the net formation of H_2 can be used as a proxy for the net formation of C-C bonds in the aerosol phase since much more H_2 is produced than can be accounted for in the chemical transformation from CH_4 to purely gas-phase hydrocarbons. For example, if all C-C bonds formed remained in gas-phase hydrocarbons, then mass balance of the measured gas-phase species would hold (equation 7)

$$\Delta[H_2] = \Delta[C_2H_6] + 2\Delta[C_2H_4] + 3\Delta[C_2H_2] + 4\Delta[C_3H_4] + 7\Delta[C_4H_2] + 3\Delta[C_4H_{10}] \quad (7)$$

where $\Delta[X]$ is the net change in concentration of species X during the irradiation, weighted by the number of C-C bonds in X. However, the data from Figure 4 demonstrate that $\Delta[H_2]$ is much greater than can be accounted for by the expression on the right-hand side of equation 7. Thus, a significant number of C-C bonds that must have formed during irradiation are not measured by the mass spectrometer and must be in particulate form. An upper limit for the number density of C-C bonds in particles, $[C-C_{\text{particles}}]$, can therefore be calculated using equation (8) using the final values for the H_2 and hydrocarbon number densities:

$$[C-C_{\text{particles}}] = [H_2] - ([C_2H_6] + 2 [C_2H_4] + 3 [C_2H_2] + 4 [C_3H_4] + 7 [C_4H_2] + 3 [C_4H_{10}]) \quad (8)$$

For the 70 Torr experiment, for example, 4.5×10^{17} molecules cm^{-3} of H_2 are produced, while the sum change in concentrations for gas phase hydrocarbons weighted by number of C-C bonds is 2.7×10^{16} C-C bonds cm^{-3} (Table 1). Thus, at the end of the irradiation period about 4×10^{17} C-C bonds cm^{-3} must be present in particles. Similarly, a proxy for the net production rate of C-C bonds in particulate form can be derived using the time-dependent values for the H_2 and hydrocarbon number densities (Figure 4h).

3.2 Optical scattering results: The time evolution of the optical scattering signal shown in Figure 7 results from light scattering by photochemically-generated particles. Potential scattering artifacts from gas phase species, such as Rayleigh scattering, rotational Raman scattering (which is effectively elastic scattering given the transmission window of the HeNe filter), and resonant fluorescence scattering in the visible by radicals would be proportional to the number density of the scattering species. Yet none of the concentration profiles of measured or inferred gas phase species match the time evolution of the scattering signal in Figure 7.

We hypothesize that the signal is the result of one or both of the following processes: (1) light is intensely scattered from spherical particles, of which a component passes through the output polarizer, or (2) light is scattered from single amorphous, fractal particles. For scenario (1), Mie theory dictates that, for incident light polarized perpendicular to the detection plane, no scattering should be detected in our experiment at $\theta=90^\circ$ [*van de Hulst*, 1957] (see Figure 5). In this case, the fact that we do see a signal would indicate that a component of the scattered light from the spherical particles passes through the output polarizer and is detected due to imperfect polarizers and/or inexact optical alignment to 90° . For scenario (2), a fractal particle may scatter light at 90° , polarized in any direction, for E_0 polarized perpendicular to the detection plane [*Lu and Sorensen*, 1994]. The preliminary SEM analysis of particles from these experiments described in section 2.4 above showed both spherical and fractal particles. Indeed, based on analyses of photometric and

polarimetric observations made by the Voyager and Pioneer spacecraft [West and Smith, 1991], as well as microphysical models [Rannou *et al.*, 1995] and some laboratory simulations [Coll *et al.*, 1999] of Titan haze, it is likely that the particles produced photochemically in Titan's atmosphere are fractal aggregates.

In an important enhancement to the instrumentation, we are currently modifying the optical scattering detection scheme to include a computer-controlled rotation stage in order to measure the angular dependence of the scattered light in the XY detection plane (i.e., as a function of θ in Figure 5 from $\theta \sim 0^\circ$ to $\sim 175^\circ$). From the angular dependence of light scattering, the size distribution and the complex index of refraction of the particles (at the wavelength of incident light) may be computed [see, e.g., Volten *et al.*, 2001; Braak *et al.*, 2001]. Until this modification is tested and calibrated--against an aerosol of known chemical composition and size distribution, for example--we estimate here a monodisperse particle size and number density that could produce the magnitude of scattering signal shown in Figure 7. Given the intensity of the incident radiation and our measurement efficiency for collecting scattered photons, assuming that the particles are fractal aggregates of hydrocarbon soot consisting of ~ 10 monomers with a depolarization ratio, p , of ~ 0.5 [Lu and Sorensen, 1994] and an index of refraction of $1.6 - i0.61$ [Markel and Shalaev, 2001], we use Mie theory to make a range of self-consistent estimates for combined particle size and number density based on Q_{sca} , the scattering efficiency of a single particle. We calculate that Q_{sca} is on the order of 10^{-4} for $0.02 \mu\text{m}$ particles, 0.4 for $0.2 \mu\text{m}$ particles, and 1.2 for particles larger than $0.6 \mu\text{m}$ in diameter. Thus, our measured scattering signal could correspond to ~ 10 particles cm^{-3} with a $1 \mu\text{m}$ diameter, 2000 particles cm^{-3} with a $0.2 \mu\text{m}$ diameter, or 10^8 particles cm^{-3} with a $0.02 \mu\text{m}$ diameter. For comparison, we note that settling velocities of about 1 cm hr^{-1} for 0.1 to $1 \mu\text{m}$ particles at a total pressure of 70 Torr are consistent with both the appearance of scattering signal at about 15 hours of irradiation in the 70 Torr CH_4 experiment (since most of the light intensity is

absorbed in the top few cm of the chamber and the laser interaction region is ~25 cm below the top of the chamber) and with decay of the signal to near zero within about 20 hours after the maximum scattering signal is observed. Taken together, the estimate of the particle properties and number density needed to produce the observed scattering signal, the indirect estimate of particle size based on settling velocities, and the preliminary offline SEM analyses of particle size and shape from the experiment are self-consistent and suggest a particle size distribution dominated by submicron particles, as should be expected for a system where gas to particle conversion is occurring.

The experiments presented here are the first to report the photochemical formation of condensed phase hydrocarbons from irradiation of pure CH₄. Previous experiments irradiating CH₄ with 123.6nm light [*Chang et al.*, 1979] or CH₄/Ar mixtures with 100-165nm light [*Bar-Nun and Podolak*, 1979] did not produce evidence for the production of particulates or films, although the sole indicator of particle production in these experiments was visual inspection of the reaction chamber and irradiation source. Chang and co-workers used a total intensity of $6 \pm 2 \times 10^{15}$ photons s⁻¹ over 6 hrs, while Bar-Nun and Podolak used 1.41×10^{14} photons s⁻¹ over 2 hrs. By comparison, we use a broader spectral output (120-300 nm) with a greater irradiation intensity ($8.8 \pm 0.8 \times 10^{15}$ photons s⁻¹) over a longer time period (70 hrs). Our detection of the production of particulates from pure CH₄ is therefore likely due to our broader spectral output, increased VUV intensity, longer irradiation times, and very high optical sensitivity, or some combination of these factors, compared with the earlier experiments.

4. Conclusions

We have developed new instrumentation for simultaneously measuring the net production rates of both particles and their gas-phase precursors driven by UV irradiation of gases or mixtures of gases simulating planetary atmospheres. To our knowledge, simultaneous, time-resolved, *in situ* measurements of aerosol and gas-phase species have not been made prior to this work.

Measurements shown here for the simplest system of CH₄ polymerizing to hydrocarbon particles under UV irradiation demonstrate our ability to monitor the kinetics of formation of aerosol particles and non-methane hydrocarbons *in situ*. Experiments can now be extended to gas mixtures that more realistically simulate planetary atmospheres, such as trace CH₄ in a H₂/He atmosphere for Saturn and Jupiter, N₂ with trace CH₄ and other gases for Titan, and mixtures of N₂, CO₂, CH₄, and H₂O for early Earth (or any terrestrial-like planet early in its evolution). With the additional modification to the apparatus to determine the angular dependence of the optical scattering from the particles, information on the size distribution and index of refraction of the aerosol (at the wavelength of incident radiation) can also be derived from the observed particle scattering matrix which will be measured *in situ* in the chamber.

The *in situ*, time-resolved measurements of the net formation rates of both gas phase hydrocarbons and particulates, as well as measurements of the index of refraction and time evolution of particle size, will improve our understanding of the mechanism of haze formation and will guide a more accurate and less parameterized representation of haze in models in general. More specifically, experiments with this apparatus will provide experimental constraints on whether or not a hydrocarbon haze could have formed on early Earth and whether it warmed or cooled the atmosphere or provided a UV-shield. From the dependence of particle formation rates on pressure and light intensity, the differences in chemical compositions among previous laboratory simulations of Titan-like particles [reviewed in McKay *et al.*, 2001] and in potential chemical and seasonal differences between the upper and lower haze layers on Titan [McKay *et al.*, 2001] may be better understood. Although the detailed conditions of planetary atmospheres (such as temperatures below 200K in Titan's atmosphere) are not realistically simulated in these experiments, data from experiments can be used to test kinetic schemes in photochemical models of planetary atmospheres [e.g., Yung *et al.*, 1984; Gladstone *et al.*, 1996] and to more rigorously define the gas-to-particle

conversion process and particulate formation rates under different conditions (e.g., UV light intensity, total pressure, gas mixing ratios, etc.). Thus, this new experimental technique provides fundamental new chemical information on aerosol formation as well as new constraints for both microphysical and photochemical models of planetary hazes.

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Table 1. Net production rates of species from the first-order model fit to the measurements.

Species	Initial Concentration (cm ⁻³)	Production Rate (cm ⁻³ s ⁻¹)
H ₂	$5.7 \cdot 10^{15}$	$9.81 \pm 0.36 \cdot 10^{11}$
C ₂ H ₂	$5.9 \cdot 10^{13}$	$2.80 \pm 0.32 \cdot 10^{10}$
C ₂ H ₄	$6.3 \cdot 10^{14}$	$3.99 \pm 8.70 \cdot 10^9$
C ₂ H ₆	$2.6 \cdot 10^{15}$	$8.44 \pm 1.10 \cdot 10^{10}$
C ₃ H ₄	$6.3 \cdot 10^{13}$	$2.30 \pm 0.77 \cdot 10^9$
C ₄ H ₂	$2.6 \cdot 10^{13}$	$5.81 \pm 3.61 \cdot 10^8$
C ₄ H ₁₀	$1.4 \cdot 10^{14}$	$1.24 \pm 0.20 \cdot 10^{10}$
C-C _{particles}	-	$7.55 \pm 0.35 \cdot 10^{11}$

Note: Units for concentration and production rates are given in molecules cm⁻³ and molecules cm⁻³ s⁻¹, respectively.

FIGURES

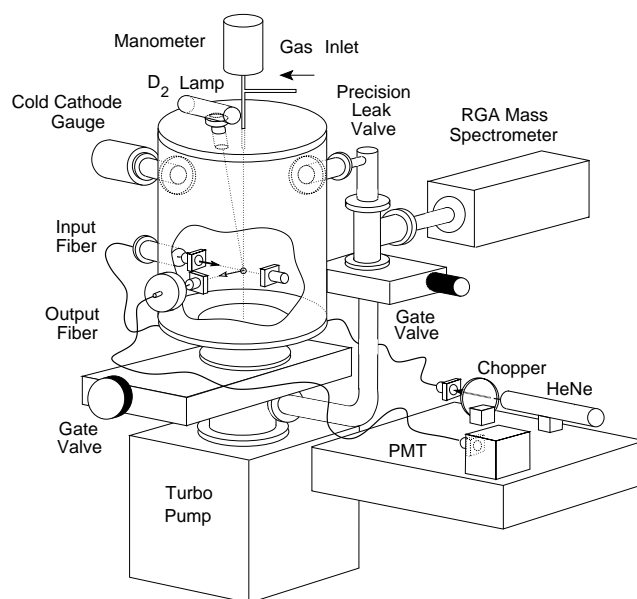


Figure 1 Experimental setup with reaction chamber, mass spectrometer, and optical scattering detection scheme.

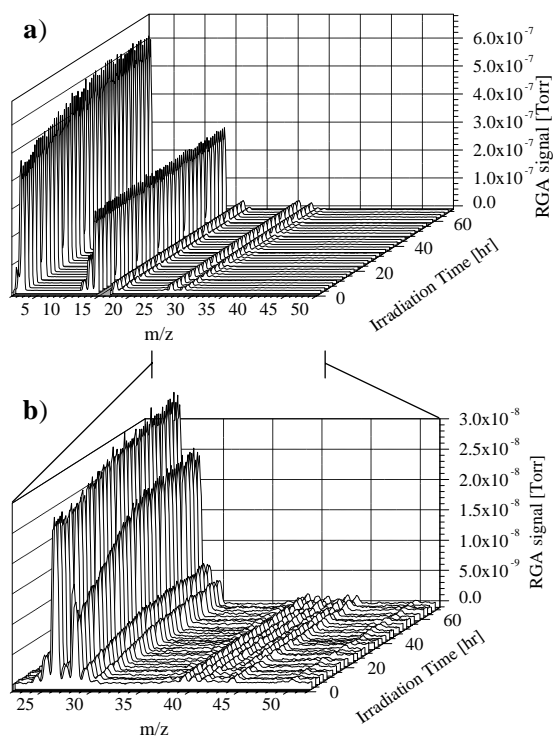


Figure 2. Time series of m/z signals as output in partial pressures (Torr) from the RGA mass spectrometer for (a) $m/z = 0$ to 50 and (b) $m/z = 23$ to 52. The CH_4 peak at $m/z=16$ has been removed for clarity.

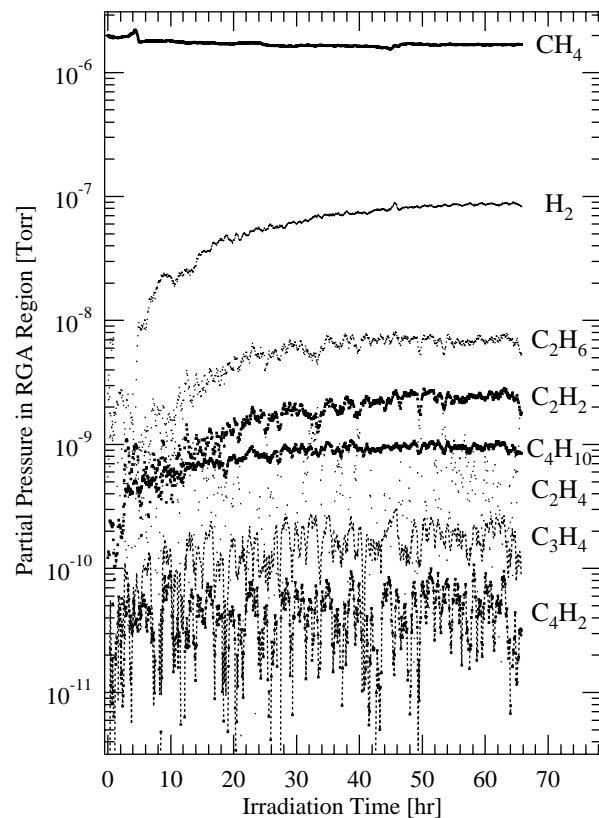


Figure 3. Calibrated partial pressures of gas-phase species in the RGA mass spectrometer after deconvolution of the electron impact fragmentation patterns (see text).

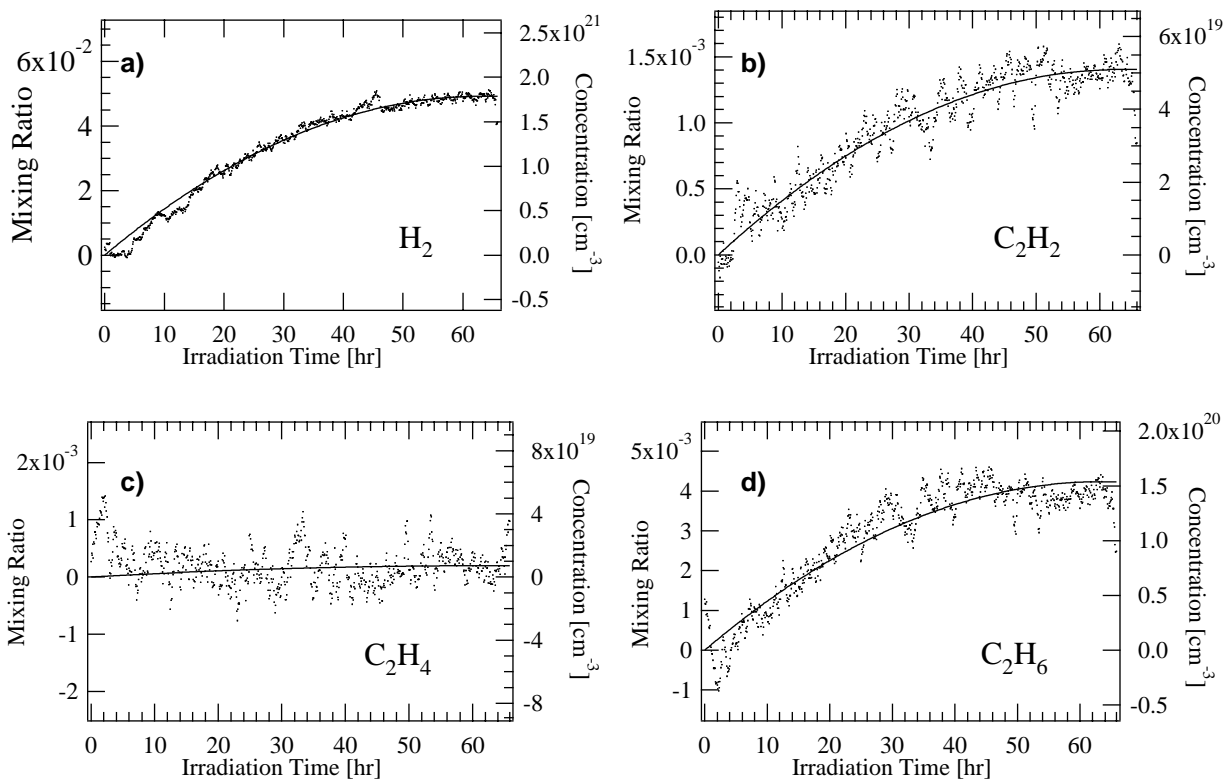


Figure 4. Time evolution of selected gas-phase species in the reaction chamber (*points*), and results of the first-order kinetics model (lines) used to deconvolve the dependence of the net production rates on the decreasing VUV intensity (see sec.3.1) .

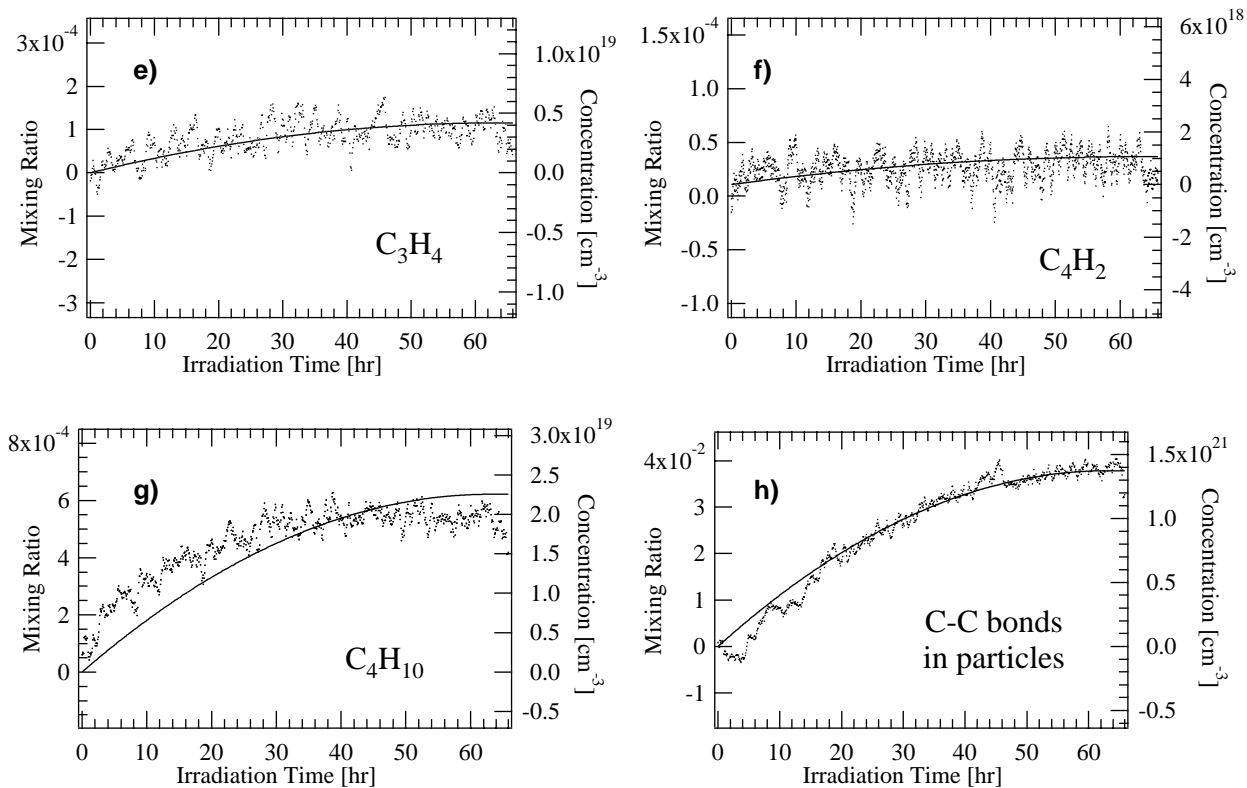


Figure 4 (continued).

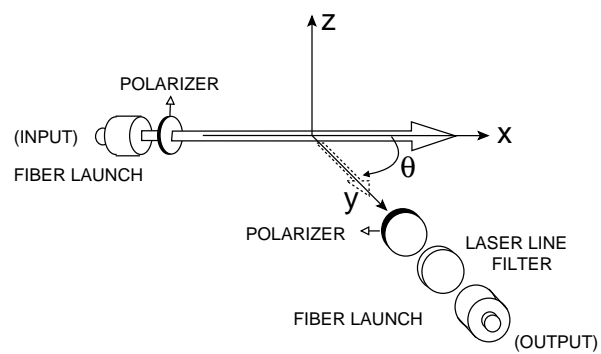


Figure 5. Scattering geometry and optics used in the experiment.

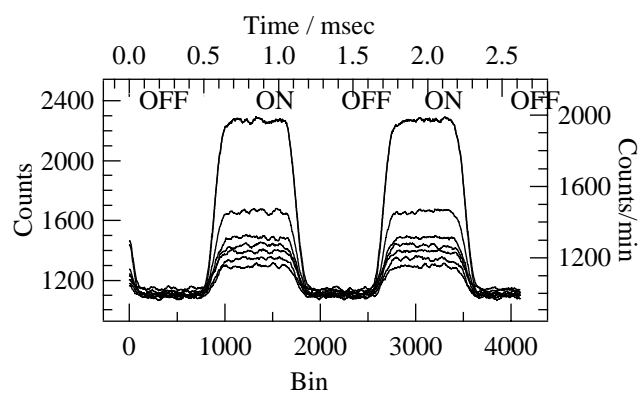


Figure 6. Raw photon-counting data for scattered light for laser "on" and "off" periods at 7 different times, t , during the ~ 60 hour VUV irradiation experiment, from $t=10\text{hr}$ (lowest count rate shown) to $t=22\text{hr}$ (highest count rate shown).

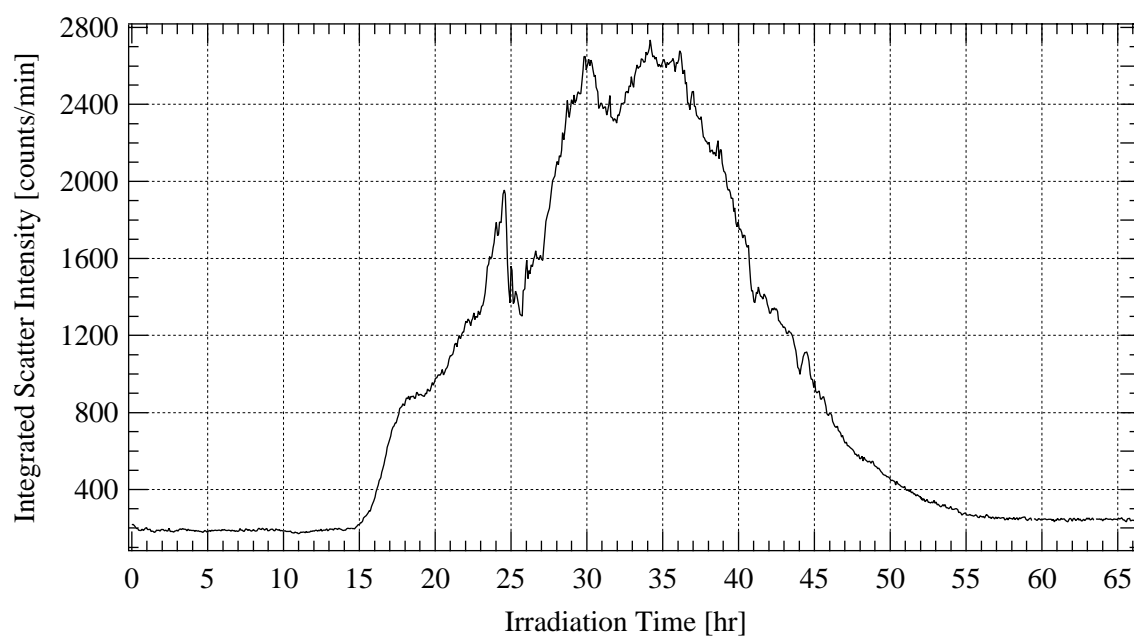


Figure 7. Optical scattering data from photochemically-generated particulates during irradiation of CH_4 at 70 Torr. Data shown were collected simultaneously with the mass spectrometer data shown in Figures 2-4.

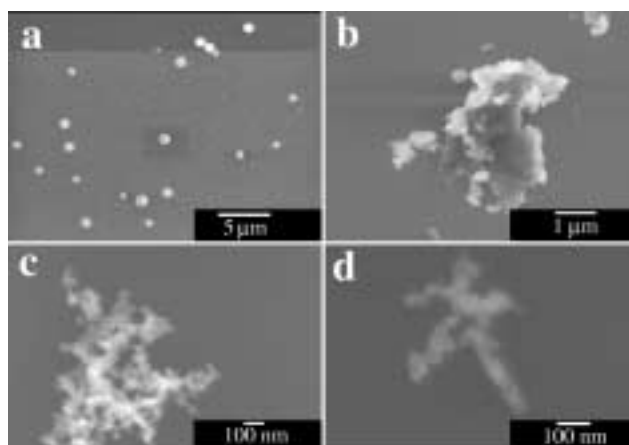


Figure 8. Field emission scanning electron microscopy of photochemically-generated particulates collected on a silicon wafer in the reaction chamber during an experimental run for pure CH_4 photolysis. The film is composed of predominantly 1-3 μm spheres (a), as well as micron-sized fractal aggregates (b), and sub-micron aggregates (c) and (d).

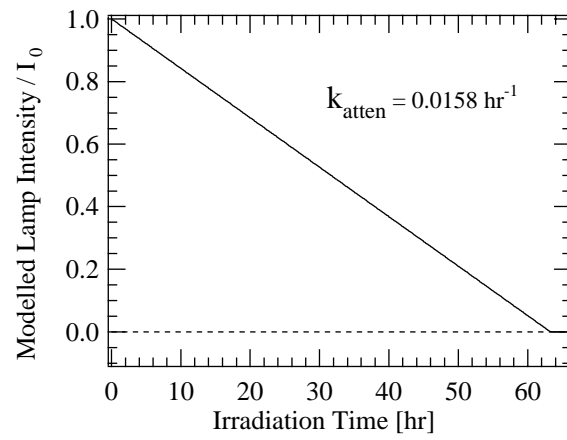


Figure 9. Modeled deuterium lamp intensity profile.